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IDENTIFICATION OF LOCAL COMPACTIONS IN CERAMICS

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Fractures of non-fired samples and samples heat-treated in the temperature range 900 – 1200°C made of a mixture of tinted granules molded at various pressure levels and non-tinted powder are investigated. It is demonstrated that a crack propagates along the boundaries of the granules simulating local compaction areas, and after firing at 1050 – 1100°C, the fracture becomes more level. At the same time, the system (the sample) passes to an unstable state which has the properties of a bifurcation. An increase in the heating rate from 2.5 to 6.5°C/min produces a shift in the transition from an uneven to a level fracture depending on the initial granule density (granule molding pressure). The identification and elimination of the principal bifurcations in a technological process opens up the possibility of developing ceramics with reproducible structure and properties.

Local compactions arising in molding, drying, or sintering of ceramics mean that consolidation (shrinkage) occurs not in the whole volume of the body but inside numerous isolated areas. The density in these areas increases and crystals start growing, whereas increased porosity can be found between these areas. The presence of large pores and crystals in a ceramic material structure significantly impairs its properties, primarily, mechanical ones.

So far, there is no reliable method of identifying local compactions. Various properties are to a certain degree sensitive to structural variations; however, as practical experience shows, this level of sensitivity is insufficient for reliable identification of local compactions employing simple instruments and methods that could be implemented in any laboratory. It is essential to develop a reliable and simple method for identifying local compactions, which does not need to be very precise (since the main purpose is to identify the tendency toward structural modifications), in order to more reliably control the structure of produced pieces. Any attempts to use the parameters of dynamic elasticity modulus, gas permeability, or electric conductivity for this purpose did not yield positive results: either no variations were observed or the obtained dependences could not be unambiguously interpreted.

It was suggested in [1] that a crack in a nonfired sample propagates along the boundaries of local compaction areas, and a compaction can be estimated by studying the fractures using a binocular magnifying glass. This was not evident, since the crack due to its fast migration in a brittle material in principle could traverse local compaction areas. Another more important hypothesis suggested that a system (a heated

article) when heated to 1000 – 1200°C passes into a bifurcation area which has a deciding effect on the course of the subsequent structural evolution of the system. The fracture in this case becomes more level, whereas before and after the bifurcation area the fracture is uneven, with hollows and elevations, which were attributed to local compactions.

There can exist several bifurcations in ceramic sintering, i.e., areas in which the probabilistic nature of the system is manifested. Let us consider the principal ones that have a significant effect on the course of the subsequent evolution of the system.

It appears that the bifurcation area identified in [1] is one of the most significant ones. A system in bifurcation acquires increased sensitivity to noises, i.e., internal fluctuations and external disturbances; therefore, it is fundamentally impossible to accurately predict its subsequent evolution. The purpose of a technology is to make the further system evolution more predictable, which is equivalent to the removal of the bifurcation. This would make it possible to attain greater reproducibility of the structure and properties of produced ceramic materials [2, 3]. The controlling actions can be internal, i.e., existing inside the system, or external, acting from the outside medium. When the bifurcation is eliminated using internal actions, this is equivalent to creating a prehistory for the system, since these actions are determined by the preceding technological stages. The role of internal actions in ceramic materials usually is played by the structural elements of the system [4].

The purpose of the present paper is to confirm or disprove the assumptions formulated in [1], employing special model experiments.

Specially prepared tinted granules of the same material were used as a local compaction model. Corundum powder

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TABLE 1

Granule content, wt. %	Sample molding pressure, MPa	Degree of nonuniform density, P_1/P_2	Three-point bending strength of samples, MPa	Size (mm) and shape of granule fragments
30	20	5	0.13 ± 0.04	0.2 – 0.3; rounded
	50	2	0.23 ± 0.02	0.2 – 0.3; mostly rounded
	100	1	0.37 ± 0.03	0.4 – 0.6; flat
50	20	5	0.09 ± 0.06	0.1 – 0.2; rounded
	50	2	0.23 ± 0.01	0.2 – 0.3; mostly rounded
	100	1	0.26 ± 0.06	Around 0.5; flat

of grade GLMK (powder with 0.25% MgO) was preliminarily tinted by an alcohol solution of ink paste and then used to produce tablets by dry-press molding at a pressure of $P_1 = 100$ MPa. The tablets were pulverized and scattered on sieves, producing granules 0.5 – 0.8 mm in size, and then mixed with non-tinted, non-granulated powder. The mixture was used to mold bars at a pressure P_2 , which varied from 0 to P_1 . The samples have different degrees of nonuniform density, which was understood as the ratio of the granule molding pressure to the molding pressure of the samples containing granules (P_1/P_2). The strength of the samples was measured by the three-point bending method, and the type of fracture was investigated using a binocular magnifying glass. The compositions of the molded articles and the testing results of the samples made of GLMK powder with granules are given in Table 1.

TABLE 2

Firing temperature, °C	Three-point bending strength of samples, MPa	Type of fracture
900	0.15 ± 0.03	Uneven, rounded granules, size 0.4 – 0.6 mm
950	0.36 ± 0.08	The same
1000	0.40 ± 0.10	Becoming level, flat granules, size ~0.5 mm
1050	0.73 ± 0.13	The same
1100	1.60 ± 0.25	The same
1150	2.00 ± 0.19	Uneven, rounded granules, size 0.4 – 0.6 mm; granular-shaped elements up to 0.1 – 1.5 mm in size
1200	3.34 ± 0.40	The same

TABLE 3

Sample	Molding pressure, MPa		Degree of nonuniform density (P_1/P_2)
	of samples (P_2)	of granules (P_1)	
1	100	400	4.0
2	200	400	2.0
3	300	400	1.3
4	400	400	1.0

The results of testing the model samples substantiate the hypothesis put forward in [1]. With a high degree of nonuniform density ($P_1/P_2 = 5$), the granule fragments visible in the fracture looked similar to the granules not introduced into the powder and differed from the matrix relief. With a low degree of nonuniform density ($P_1/P_2 = 1$), the size of the granule fragments approximated the size of the granules themselves, and their relief did not differ from the matrix relief. That is, if a sample contained denser areas, the crack in the course of its destruction propagated along the denser area boundaries. This means that the presence or absence of local compactions can be inferred from the sample fracture studied under a microscope.

It was more difficult to prove the existence of a main bifurcation area in the temperature region 1000 – 1200°C. According to the data in [1], the fracture in the bifurcation area becomes smoother, whereas before and after this area the fracture is rough due to local compactions. This is the area where the effect of the preceding local compactions is weakened, and the system selects a controlling action for the subsequent evolution. Such action can be an internal signal, i.e., the effect of the structural elements created at preceding stages (a prehistory), which is equivalent to the removal of the bifurcation. In this way, heat-resistant but more dense refractories are formed using incompletely sintered granules as the large-size fraction [5]. In sintering of a sample, the granules become consolidated while preserving their individuality and form a coarse-grained fraction in the refractory. Another option for the system is to preserve the bifurcation and manifest a probabilistic nature in selecting a new structure. It can be said that while the bifurcation is preserved, the controlling action is probabilistic (stochastic). In such a case, the prehistory memory is erased, and it is fundamentally impossible to reproduce the emerging structures.

It is possible to control the system in the bifurcation area using external actions. The simplest way of modifying the degree of the system nonequilibrium in the bifurcation area was to modify the sample heating rate. It is known that an increase in the degree of nonequilibrium produces a decrease in the size of the system structural element [6, 7]. A hypothesis suggests that a system in the bifurcation area transmits internal information via waves [8]. Most likely, these are the autowaves known in physics [9]. This can account for the remote effect observed in systems which transit a bifurcation from one dynamically stable state to another. Such waves play a deciding role in self-organization processes. As the degree of nonequilibrium increases, the amplitude of these waves becomes greater and exceeds the noise level (i.e., the autowaves become a controlling signal), and the period characterizing the size of the structural element decreases.

In order to prove that the leveling of the fracture relief observed within a certain temperature interval is in fact a bifurcation, it was decided to influence the subsequent evolution of the system through an external action. It was decided to increase the degree of nonequilibrium by accelerating the temperature rise while heating the samples. The idea of the experiment was derived from the assumption that if this was indeed a bifurcation

area, an increase in the process nonequilibrium should produce a situation where the controlling signal would be sent by autowaves arising in the system due to the external factor (the rate of temperature rise) rather than the internal factors (in our case, the size and density of the granules). With an increasing rate of temperature rise in the bifurcation area, the signal should be intensified as well. By producing samples with different levels of the internal signal (the granule molding pressure), it will be possible to observe the variations in the ratio of the internal signal to the signal emitted by autowaves.

First, it was necessary to identify the bifurcation area for the samples of GLMK corundum powder molded at 100 MPa, which bifurcation, according to the data in [1], was within the temperature region between 1000 and 1100°C. In order to obtain tinted granules, the powder was first impregnated with chromium chloride and heat-treated at a temperature of 1300°C. Next, the powder was subjected to wet grinding in a planetary mill for 3 min. The same as in the previous case, the tinted powder produced granules 0.5–0.6 mm in size. Tinted granules in an amount of 30% were mixed with non-tinted powder, and bars were molded of the mixture at 100 MPa ($P_1/P_2 = 1$). The samples were heat-treated within the temperature interval 900–1200°C. The strength of the samples was determined in three-point bending, and fractures were studied using a binocular magnifying glass. The experimental results are given in Table 2.

The presence of tinted granules revealed more clearly the variations in the type of fracture. Within the temperature range 1150–1100°C, the crack starts passing through via compactions, and the fracture becomes smoother. The specified temperature interval virtually coincides with the interval of 1000–1100 obtained in [1]. Apparently, this is the main bifurcation region which determines the future structure of the article. Subsequent heat treatment causes the emergence of secondary larger compactions with weakened boundaries, along which the crack starts propagating. The fracture again becomes uneven, which is also noted in [1].

With the aim of verification, two series of samples with a different degree of nonuniform density (P_1/P_2) were prepared in accordance with the previous method. The content

TABLE 4

Series	Rate of temperature rise, °C/min	Degree of nonuniform density (P_1/P_2)	Bending strength of samples, MPa	Type of fracture
1.1	3.5	4.0	0.281 ± 0.005	Uneven, rounded granules, size 0.3–0.4 mm
1.2	3.5	2.0	0.306 ± 0.013	The same, 0.3–0.5 mm
1.3	3.5	1.3	0.649 ± 0.028	Even, flat granules, size 0.3–0.6 mm
1.4	3.5	1.0	1.050 ± 0.021	The same, 0.4–0.7 mm
2.1	6.5	4.0	0.565 ± 0.075	Uneven, rounded granules, size 0.4–0.6 mm
2.2	6.5	2.0	0.952 ± 0.090	Even, flat granules, size 0.3–0.6 mm
2.3	6.5	1.3	1.751 ± 0.516	The same, 0.4–0.7 mm
2.4	6.5	1.0	3.497 ± 0.337	The same, 0.4–0.7 mm

of granules in all samples was 30%. The closer the ratio P_1/P_2 to 1, the lower the intensity of the internal controlling signals in the bifurcation area and, accordingly, the influence of the prehistory. The compositions of these series of samples are given in Table 3. The heat-treatment temperature was 1080°C, which is approximately in the middle of the unstable-state area determined on the basis of the results given in Table 2. The first series of samples was heated at a rate of 6.5°C/min, and the second one at a rate of 3.5°C/min. The data on the types of fracture and the bending strength of the samples are given in Table 4 and Fig. 1.

The obtained results, in our opinion, confirmed the above-stated assumptions. It can be seen from Table 4 that the transition from uneven to even fracture surface under a heating rate of 3.5°C/min occurred as P_1/P_2 varied from 2.0 to 1.3, and at 6.5°C/min this transition took place as the specified ratio ranged from 4.0 to 2.0. The higher the degree of nonequilibrium, the higher the amplitude of the autowaves in the bifurcation area. With a heating rate of 5.5°C/min, the autowave amplitude starts exceeding the signal sent by the structural elements even when $P_1/P_2 = 2.0$. A decrease in the nonequilibrium degree (heating rate 3.5°C/min) reduces the amplitude of the autowaves, and they start exceeding the internal signal only at $P_1/P_2 = 1.3$. This behavior of the system is also substantiated by strength variations (Fig. 1).

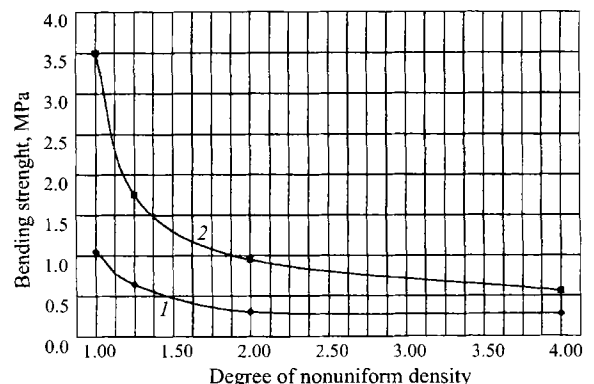


Fig. 1. Bending strength of samples versus the degree of nonuniform density in firing at a rate of 3.5°C/min (1) and 6.5°C/min (2).

The strength begins an intense increase upon the transition to a level fracture surface. The lower the extent of the nonuniform density in an unfired article, the more substantial the self-organizing effect of the autowaves. At the same time, as the degree of the process nonequilibrium increases, the autowave amplitude increases and its period decreases, which produces a decrease in the size of the structural elements arising in the course of self-organization. [3, 4, 7]. This results in a perceptible increase in the strength of the samples. That is why the highest increase in strength was observed in samples heat-treated with a heating rate of $6.5^{\circ}\text{C}/\text{min}$, and the maximum strength in both series was attained with a nonuniform density of $P_1/P_2 = 1$.

The model experiments confirmed the data presented in [1]. The crack in the fractures propagated along the boundaries of the tinted granules, simulating local compactions. After firing at $1050 - 1100^{\circ}\text{C}$, the fracture became more level, and the crack started traversing the tinted areas. This area had the attributes of a bifurcation. It is possible to use the rate of sample heating as an external signal in order to eliminate the bifurcation. This is the foundation for the positive effect of superfaster sintering on the structure of samples [10].

Thus, the study of fractures even using a simple binocular magnifying glass makes it possible to identify the presence and approximate the size of local compactions. The evolution of local compactions in heating, which can be easily inferred from the type of fracture, makes it possible to identify the main bifurcation area. It is necessary to remove the bifurcation precisely in this area, using external or inter-

nal (prehistory of the material, results of preceding technology stages) controlling actions, in order to make the subsequent evolution of the ceramic structure more predictable, especially in using highly disperse powders [1]. This opens the way toward improving the reproducibility of the structure and properties of ceramic materials.

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